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Published in:
Journal of the American Chemical Society

DOI:
[10.1021/ja054352n](https://doi.org/10.1021/ja054352n)

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Document Version
Final author's version (accepted by publisher, after peer review)

Publication date:
2005

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Citation for published version (APA):

Eelkema, R., & Feringa, BL. (2005). Macroscopic expression of the chirality of amino alcohols by a double amplification mechanism in liquid crystalline media. *Journal of the American Chemical Society*, 127(39), 13480-13481. <https://doi.org/10.1021/ja054352n>

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Supporting Information

Macroscopic expression of the chirality of aminoalcohols by a double amplification mechanism in liquid crystalline media

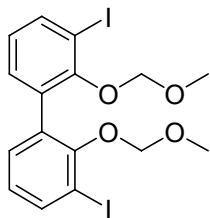
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Synthesis

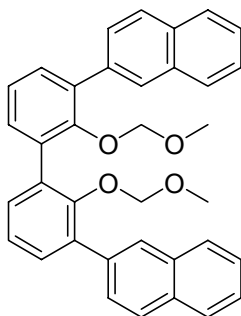
General remarks: Reagents were purchased from Aldrich, Acros Chimica, Strem, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. Chromatography: silica gel, Merck type 9385 230-400 mesh, TLC: silica gel 60, Merck, 0.25 mm. Mass spectra (HRMS) were recorded on an AEI MS-902. Melting points were recorded on a Büchi B-545 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200, a Varian VXR-300 or a Varian Mercury Plus, operating at 199.97, 299.97 and 399.93 MHz, respectively, for the ^1H nucleus, and at 50.29, 75.43 and 100.57 MHz for the ^{13}C nucleus, in CDCl_3 , unless stated otherwise. Chemical shift values are denoted in δ values (ppm) relative to residual solvent peaks (CHCl_3 , ^1H δ = 7.26, ^{13}C δ = 77.0).

3,3'-Diiodo-2,2'-bis-methoxymethoxy-biphenyl, S1



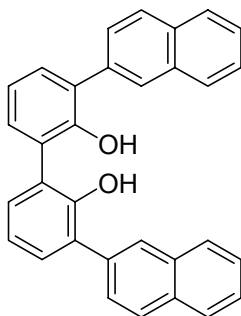
n-Buli (15.5 ml, 1.6 M in hexanes) was added dropwise to a solution of TMEDA (2.88 g, 24.8 mmol) in ether (150 ml). After stirring for 10 min 2,2'-bis-methoxymethoxy-biphenyl (2.06 g, 7.5 mmol) was added and the mixture was heated at reflux for 1.5 h, during which it became turbid. Subsequently, the mixture was cooled to -78°C and solid iodine (5.71 g, 22.5 mmol) was added. The mixture was allowed to warm to room temperature overnight, and after the addition of water (30 ml), the product was extracted with CH₂Cl₂ (3 x 30 ml), the combined organic layers were washed with brine and dried over Na₂SO₄. After evaporation of the solvent, the crude product was purified by column chromatography (SiO₂, pentane : Et₂O = 15 : 1) and subsequent recrystallization from toluene, yielding colorless crystals (3.1 g, 79%). Melting point 121.0-122.1°C. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, *J*₁ = 8.07 Hz, *J*₂ = 1.46 Hz, 2H), 7.35 (dd, *J*₁ = 7.52 Hz, *J*₂ = 1.47 Hz, 2H), 6.93 (dd, *J*₁ = 7.70 Hz, *J*₂ = 7.70 Hz, 2H), 4.80 (s, 4H), 3.03 (s, 6H). ¹³C NMR (50.32 MHz, CDCl₃) δ 154.8, 139.4, 133.4, 132.3, 125.8, 99.7, 92.9, 57.2. MS (EI): *m/z* 526 (M⁺, 3%), HRMS calcd for C₁₆H₁₆O₄I₂: 525.914; Found 525.914. Anal. Calcd. for C₁₆H₁₆O₄I₂: C, 36.53; H, 3.07%. Found: C, 36.52; H, 3.04%.

3,3'- Di-naphthalen-2-yl -2,2'-bis-methoxymethoxy-biphenyl, S2



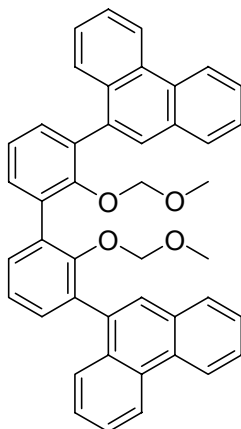
To a solution of **S1** (1.00 g, 1.9 mmol) and Pd(PPh₃)₄ (44 mg, 0.038 mmol) in dry DME (25 ml) was added an aqueous Na₂CO₃ solution (2M, 5.7 ml) and 2-naphthylboronic acid (1.31 g, 7.6 mmol). The mixture was thoroughly degassed and refluxed overnight. After allowing the reaction mixture to cool to room temperature, water (20 ml) and CHCl₃ (20 ml) were added and the layers were separated. The water layer was extracted with CHCl₃ (2 x 30 ml) and the combined organics were washed with brine. After drying over Na₂SO₄ and concentration, the crude product was purified by column chromatography (SiO₂, pentane : Et₂O = 6 : 1) and subsequent recrystallization from toluene / hexane (1/1), affording **S2** as a white solid (820 mg, 82%). Melting point 134.0-134.6°C. ¹H NMR (400 MHz, CDCl₃) 8.07 (d, *J* = 1.1 Hz, 2H), 7.94-7.90 (m, 6H), 7.84 (dd, *J*₁ = 8.59 Hz, *J*₂ = 1.47 Hz, 2H), 7.57-7.48 (m, 8H), 7.33 (dd, *J*₁ = 7.70 Hz, *J*₂ = 7.70 Hz, 2H), 4.49 (s, 4H), 2.67 (s, 6H). ¹³C NMR (100.57 MHz, CDCl₃) δ 152.6, 136.6, 135.8, 133.6, 133.4, 132.4, 131.7, 130.8, 128.1, 128.1, 128.0, 127.6, 127.6, 126.1, 125.9, 124.2, 98.9, 56.3. MS (EI): *m/z* 526 (M⁺, 7%), HRMS calcd for C₃₆H₃₀O₄: 526.214; Found 526.213. Anal. Calcd. for C₃₆H₃₀O₄: C, 82.11; H, 5.74%. Found: C, 81.93; H, 5.80%.

3,3'-Di-naphthalen-2-yl-biphenyl-2,2'-diol, 1



A solution of **S2** (500 mg, 0.95 mmol) and concentrated hydrochloric acid (1.9 ml) in THF/MeOH (4/1, 10 ml) was stirred at room temperature for 4 days. After addition of water and CH₂Cl₂ the layers were separated and the water layer was extracted three times with CH₂Cl₂. The combined organics were washed with brine, dried over Na₂SO₄ and after evaporation of the solvent the product was purified by column chromatography (SiO₂, pentane : Et₂O = 6 : 1) and subsequent recrystallization from toluene, yielding a white solid (333 mg, 80%). Melting point 179.0-180.2°C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 1.1 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.90-7.87 (m, 4H), 7.70 (dd, *J*₁ = 8.31 Hz, *J*₂ = 1.71 Hz, 2H), 7.54-7.47 (m, 6H), 7.41 (dd, *J*₁ = 7.7 Hz, *J*₂ = 1.47 Hz, 2H), 7.19 (t, *J* = 7.70 Hz, 2H), 5.94 (s, 2H). ¹³C NMR (50.32 MHz, CDCl₃) δ 149.9, 134.9, 133.5, 132.6, 131.1, 130.8, 129.5, 128.4, 128.1, 128.1, 127.7, 127.5, 126.4, 126.2, 125.1, 121.5. IR (C₆H₅CN) ν (cm⁻¹): 3647, 3526, 3401, 3059, 1599, 1443, 1325, 1221. MS (EI): *m/z* 438 (M⁺, 100%). HRMS calcd for C₃₂H₂₂O₂: 438.162; Found 438.165. Anal. Calcd. for C₃₂H₂₂O₂·0.2 H₂O: C, 86.93; H, 5.11%. Found: C, 86.93; H, 5.07%.

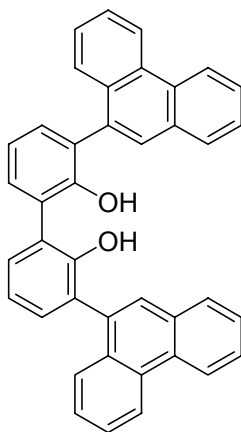
3,3'- Di-phenanthren-9-yl -2,2'-bis-methoxymethoxy-biphenyl, S4



A solution of 9-bromophenanthrene (6.46 g, 25.1 mmol) in THF (500 ml) was cooled to $-80\text{ }^{\circ}\text{C}$ and *n*-BuLi (17.3 ml, 1.6M in hexanes) was added dropwise. This mixture was stirred at $-80\text{ }^{\circ}\text{C}$ for 3 h, during which it became a yellow suspension. A ZnCl_2 solution (23.5 ml, 1.5M in THF) was added and the mixture became colorless. It was allowed to warm up to room temperature, and stirring was continued for an additional 1 h. To this solution **S1** (3.30 g, 6.29 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (72.7 mg, 0.063 mmol) were added and the resulting yellow solution was heated at reflux overnight. The resulting mixture was cooled to room temperature, water and CH_2Cl_2 were added and the layers were separated. The water layer was extracted three times with CH_2Cl_2 , and the combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (SiO_2 , pentane : Et_2O = 15 : 1), affording **S4** as a white powder (2.80 g, 71%). Melting point $104.9\text{--}106.6^{\circ}\text{C}$. **S4** appears to exist as a mixture of isomers at room temperature, judging from ^1H and ^{13}C NMR. ^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, $J = 9.17\text{ Hz}$, 2H), 8.75 (d, $J = 10.26\text{ Hz}$, 2H), 7.94–7.93 (m, 2H), 7.88–7.83 (m, 4H), 7.71–7.63 (m, 8H), 7.62–7.51 (m, 2H), 7.44–7.41 (m, 2H), 7.38–7.34 (m, 2H), 4.53 (dd, $J_1 = 17.97\text{ Hz}$, $J_2 = 6.24\text{ Hz}$, 2H), 4.45–4.43 (m, 2H), 2.50 (s, 6H). ^{13}C

NMR (50.32 MHz, CDCl₃) δ 153.18, 153.15, 135.70, 135.51, 134.53, 133.31, 133.22, 131.98, 131.78, 131.72, 131.44, 131.43, 131.36, 131.22, 130.34, 130.26, 130.05, 130.01, 128.67, 128.43, 128.40, 127.34, 127.16, 126.71, 126.60, 126.42, 123.88, 123.78, 122.65, 122.59, 122.52, 98.69, 98.60, 56.17. MS (EI): m/z 626 (M^+ , 16%). HRMS calcd for C₄₄H₃₄O₄: 626.246; Found 626.250. Anal. Calcd. for C₄₄H₃₄O₄·0.25 H₂O: C, 83.72; H, 5.51%. Found: C, 83.59; H, 5.42%.

3,3'-Di-phenanthren-9-yl-biphenyl-2,2'-diol, 2



A solution of **S4** (220 mg, 0.35 mmol) and concentrated hydrochloric acid (0.7 ml) in CH₂Cl₂/MeOH (3/1, 4 ml) was stirred at room temperature for 4 days. After addition of water and CH₂Cl₂ the layers were separated and the water layer was extracted three times with CH₂Cl₂. The combined organics were washed with brine, dried over Na₂SO₄ and after evaporation of the solvent the product was purified by column chromatography (SiO₂, pentane : Et₂O = 6 : 1) and subsequent recrystallization from toluene, yielding a white solid (160 mg, 85%), which, judging from ¹H and ¹³C NMR, exists as a mixture of isomers at room temperature. Melting point 250.4-251.9°C. ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, J = 8.49 Hz, 2H), 8.73 (d, J = 8.31 Hz, 2H), 7.89 (d, J = 7.90 Hz, 2H), 7.80 (s,

2H), 7.76-7.73 (m, 2H), 7.71-7.57 (m, 8H), 7.53-7.48 (m, 2H), 7.42 (dd, $J_1 = 7.46$ Hz, $J_2 = 1.69$ Hz, 2H), 7.27-7.23 (m, 2H), 5.83 (s, 1H), 5.76 (s, 1H). ^{13}C NMR (100.57 MHz, CDCl_3) δ 150.41, 150.35, 133.60, 133.59, 131.76, 131.42, 131.41, 131.31, 131.27, 130.89, 130.87, 130.58, 130.57, 130.33, 128.78, 128.78, 128.71, 128.70, 128.12, 128.07, 126.99, 126.92, 126.91, 126.89, 126.81, 126.67, 126.63, 125.71, 125.60, 122.93, 122.56, 121.38, 121.34. IR ($\text{C}_6\text{H}_5\text{CN}$) ν (cm^{-1}): 3649, 3538, 3381, 3023, 1624, 1434, 1321, 1228. MS (EI): m/z 538 (M^+ , 100%). HRMS calcd for $\text{C}_{40}\text{H}_{26}\text{O}_2$: 538.193; Found 538.191. Anal. Calcd. for $\text{C}_{40}\text{H}_{26}\text{O}_2 \cdot 0.5 \text{H}_2\text{O}$: C, 87.73; H, 4.97%. Found: C, 87.59; H, 4.85%.

Measurements

General experimental remarks: all solvents were HPLC or spectroscopic grade, and were used as received. The liquid crystalline material E7 was received as a gift from Merck, Darmstadt.

General procedure for determination of the cholesteric pitch.

The pitch of the liquid crystalline (LC) phases was determined by Grandjean-Cano technique,ⁱ using plane-convex lenses of known radii ($R = 25.119$ or 30.287 mm, Linos Components; Radiometer), and an Olympus BX 60 microscope equipped with a Linkam THMS 600 hotstage. LC phases were aligned on a glass surface (typically 6.25 cm^2) that was spin-coated with commercially available polyimide AL1051 (purchased from JSR, Belgium) and linearly rubbed with a velvet cloth. Using stock solutions of amines and biphenols in CH_2Cl_2 , mixtures of these two compounds were made. The CH_2Cl_2 was removed under reduced pressure, and E7 (stock solution in toluene) was added. This solution was applied on a linearly rubbed, polyimide-coated glass plate and after the toluene had evaporated in the air, the glass plate was put under the microscope. After applying a plane-convex lens of known diameter, Grandjean-Cano lines could be

observed in the described cases, and the pitch could be determined by measuring the distances between the consecutive lines. When, as a control experiment, mixtures of E7 with biphenols **1** or **2** or aminoalcohols (S)-**3** or (S)-**4** were made, no cholesteric textures or Grandjean-Cano lines were observed. To check if the difference in pitch as described in Table 1 was not a result of a difference in clearing temperature between the complexes, the clearing temperatures of mixtures of E7 with complexes **1•3**, **1•4**, **2•3** and **2•4** were determined. In all four cases the same clearing temperature was observed ($T_c = 57.6 \pm 0.2$ °C). As the clearing temperature of E7 with only aminoalcohols **3** or **4** ($T_c = 59.5 \pm 0.1$ °C), is higher than for the complexes the lack of cholesteric induction by the sole aminoalcohols can not be ascribed to a depression in clearing temperature. The sign of the helical pitch was determined with a contact method,ⁱⁱ where mixing of the samples with a doped cholesteric liquid crystal of known negative screw sense, consisting of dopant ZLI-811 (Merck, Darmstadt, Germany) in E7, was tested.

2D NOESY of **1•3**.

The 2D NOESY spectrum of **1•3** was recorded at 400MHz, using a mixture of **1** (0.046M) and **3** (0.265M) in CDCl₃. The mixing time was set to 0.7 s. In the areas surrounded by the dotted lines the interactions between the naphthalene protons of **1** and the aliphatic protons of **3** are visible.

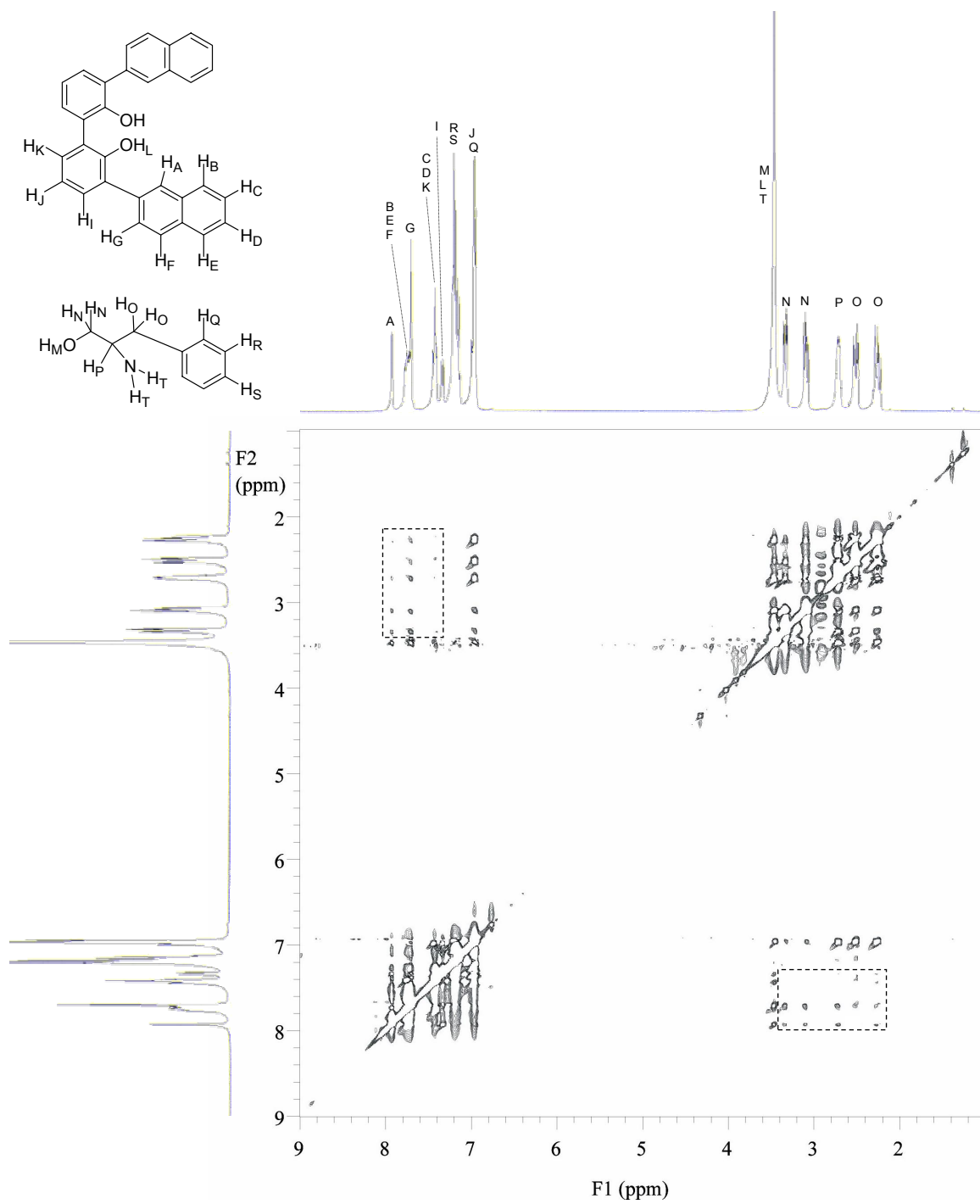


Figure S1. 2D NOESY spectrum of **1•3**.

Job's plot analysis of **1•3**.

The 1:1 binding stoichiometry of the **1•3** complex was confirmed as follows. Stock solutions of **1** (0.04 M in CDCl₃) and (*S*)-**3** (0.04 M) were prepared, and seven NMR tubes were filled with solutions of **1** and **3** in the following volume ratios: 400:100, 375:125, 333:167, 250:250, 167:333, 125:375, 100:400 μ L. ¹H NMR spectra were recorded at 400 MHz for each mixture. The monitored chemical shift is of the Q-phenyl protons of **3**.

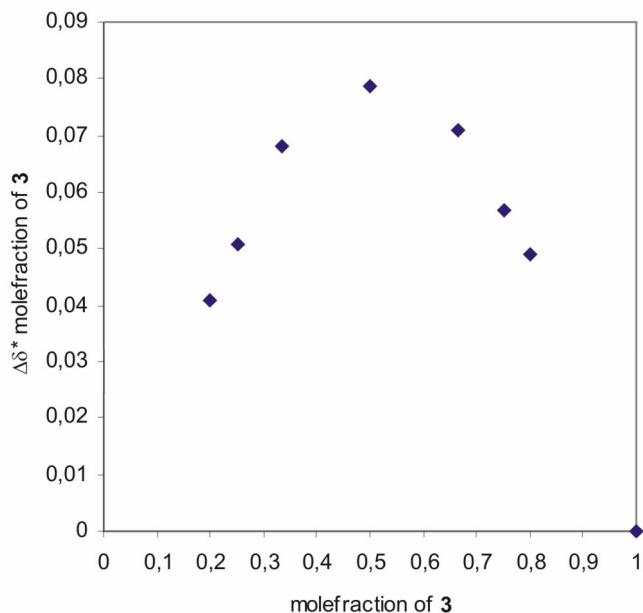


Figure S2. Job's plot to prove the binding stoichiometry of **1•3**.

FTIR hydrogen bond motif determination of **1•3**.

IR spectra were recorded on a Thermo Nicolet Nexus FTIR spectrometer, using HPLC grade benzonitrile. 1:1 ratio solutions of **1•3** of known concentration (0.01M, 0.025M, 0.05M, 0.1M, 0.15M, 0.2M) were used, and the stretching vibrations of free OH (3650 cm⁻¹) and hydrogen-bonded OH (3600-3200 cm⁻¹) were monitored, showing an

increasing absorption of hydrogen-bonded OH, whereas the free OH remained almost constant, pointing towards an incorporation of all OH groups in the complex. This motif has been reported in literature.ⁱⁱⁱ

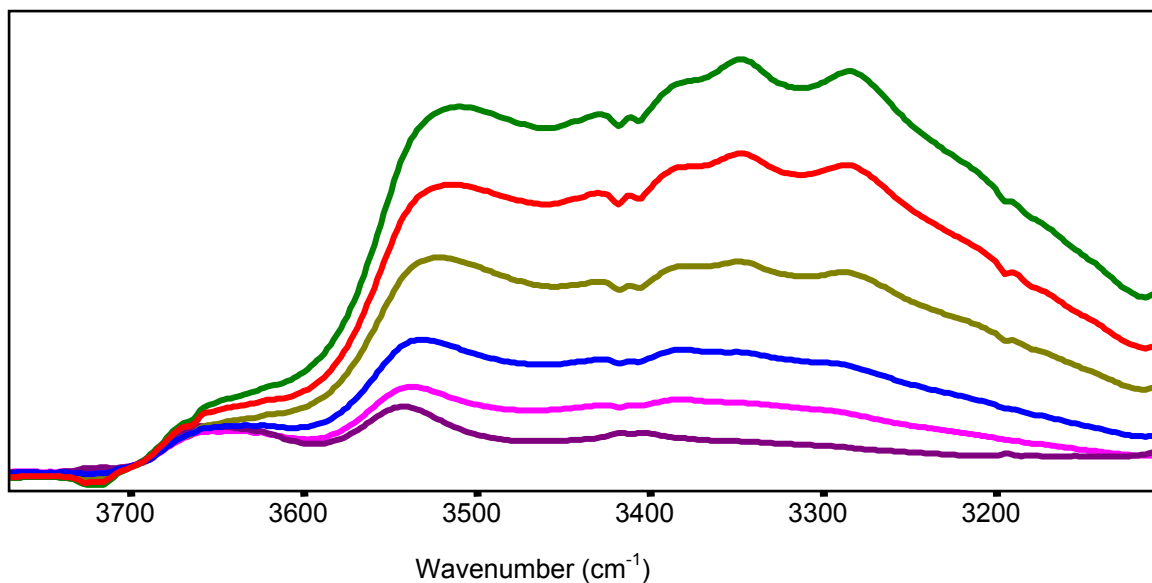


Figure S3. FTIR of **1•3** at different concentrations: 0.01M (dark violet line), 0.025M (pink) , 0.05M (blue), 0.1M (olive), 0.15M (red), 0.2M (green).

Circular dichroism of **1•3**.

CD spectra were recorded on a JASCO J-715 spectropolarimeter and UV measurements were performed on a Hewlett-Packard HP 8453 FT spectrophotometer using UVASOL grade CHCl_3 (Merck) in a 1.0-mm quartz cell at ambient temperature (20-25°C). For both, $[\mathbf{1}] = 4.04 \times 10^{-4} \text{ M}$, $[\mathbf{3}] = 0.202 \text{ M}$ (500 eq.).

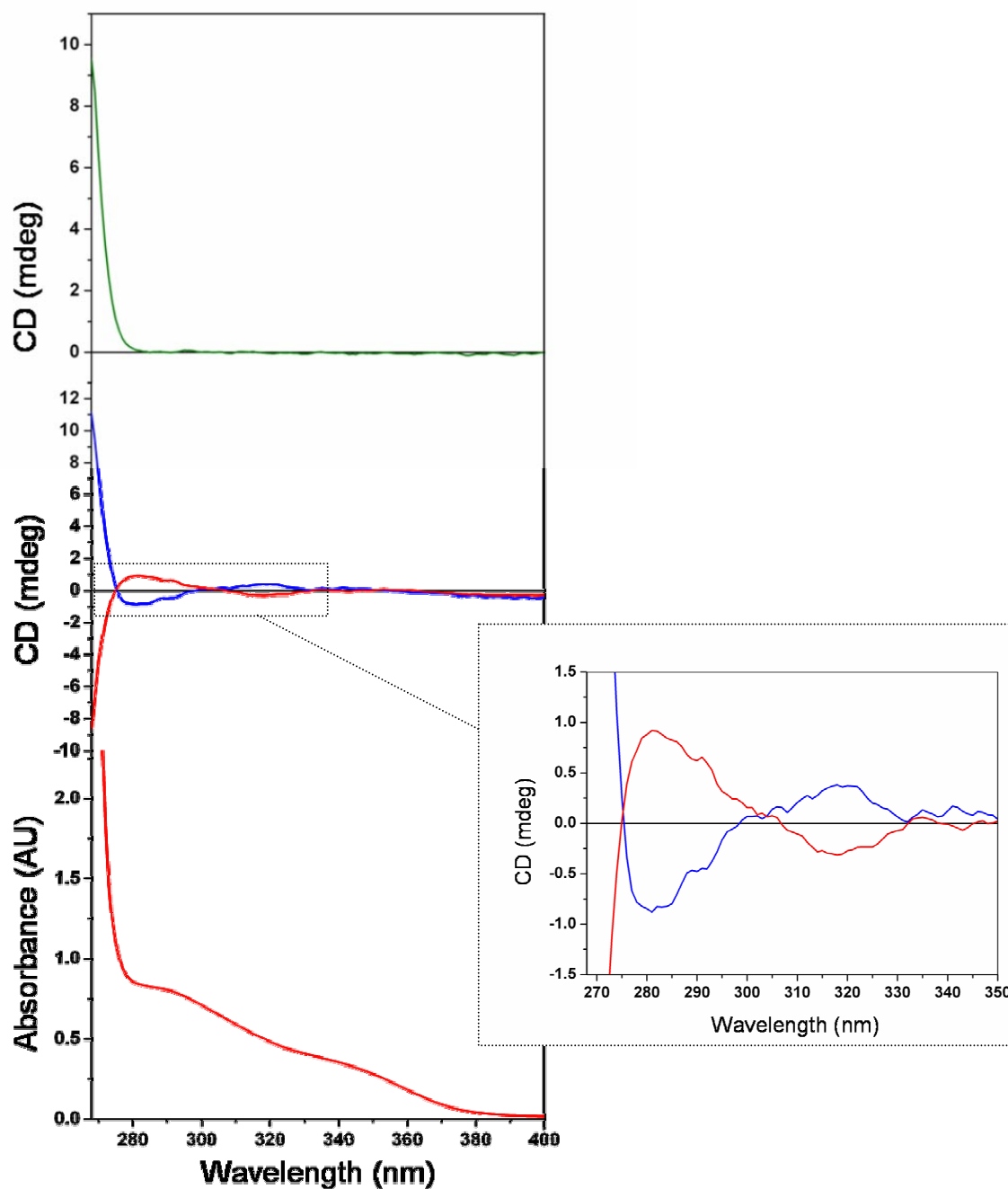


Figure S4. CD spectra of (*S*)-**3** (green line), **1•(S)-3** (red line), **1•(R)-3** (blue line) and the UV of **1•(S)-3** (red line). The inset shows an enlarged part of the CD spectra of **1•(S)-3** (red line) and **1•(R)-3** (blue line).

ⁱ Heppke, G.; Oestreicher, F. *Mol. Cryst. Liq. Cryst.* **1977**, *41*, 245-249.

ⁱⁱ Isaert, N., Soulestin, B., Malthète, J. *Mol. Cryst. Liq. Cryst.* **1976**, *37*, 321–333.

ⁱⁱⁱ Wojciechowski, G., Schroeder, G., Zundel, G., Brzezinski, B. *J. Phys. Chem. A* **2000**, *104*, 7469-7472.